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HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF CERIUM DIOXIDE AND COLUMBIUM DIOXIDE

By E. G. King and A. U. Christensen

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

(1961)

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* * * * * report of investigations 5789

UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the Office of Naval Research, U.S. Department of the Navy.

This publication has been cataloged as follows:

King, Edward G

High-temperature heat contents and entropies of cerium dioxide and columbium dioxide, by E. G. King and A. U. Christensen. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1961]

6 p. illus., tables. 26 cm. (U.S. Bureau of Mines. Report of investigations, 5789)

Based on work done in cooperation with the Office of Naval Research, U.S. Dept. of the Navy.

Bibliographical footnotes.

1. Cerium dioxide. 2. Columbium dioxide. 3. Entropy. I. Christensen, A U joint author. II. Title. (Series)

TN23.U7 no. 5789 622.06173

U.S. Dept. of the Int. Library.

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HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF CERIUM DIOXIDE AND COLUMBIUM DIOXIDE^{1/}

by

E. G. King^{2/} and A. U. Christensen^{3/}

INTRODUCTION AND SUMMARY

This report contains experimentally determined heat-content values for cerium dioxide and Columbium (niobium) dioxide in the temperature range from 298° to 1,800° K. There are no previous similar data for Columbium dioxide, and those for cerium dioxide have an upper limit of 373° K.

The heat-content and corresponding entropy-increment data are presented in tabular form. Equations were derived to represent the heat contents and heat capacities.

The data for cerium dioxide are entirely regular, but those for columbium dioxide show two previously unreported anomalies at 1,090° and 1,200° K.

MATERIALS

Columbium dioxide was prepared from high-purity columbium pentoxide obtained from Fansteel Metallurgical Corp. Small batches of the pentoxide were reduced in hydrogen for 4 hours at 950° to 1,000° C., and then combined and given 4 hours more treatment in hydrogen at the same temperature. The completeness of the reduction reaction was demonstrated by heating part of the product in hydrogen at 1,450° C. and observing that there was no change in weight. Analysis of the product by reversion to the pentoxide indicated 99.90 percent columbium dioxide. Analysis by dissolving, precipitating the columbium as hydroxide, and igniting to constant weight showed virtually 100 percent columbium dioxide. The X-ray diffraction pattern matched that of Brauer,^{4/} who prepared his sample similarly.

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^{1/} Work on manuscript completed October 1960.

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^{4/} Brauer, G., Die Oxyd des Niobs: Ztschr. anorg. allgem. Chem., vol. 248, 1941, p. 1.

Cerium dioxide having a claimed purity of 99.9+ percent was obtained from the Lindsay Chemical Division of American Potash & Chemical Corp. It was used without treatment, except heating at 1,050° C. for 1 hour.

MEASUREMENTS AND RESULTS

The high-temperature heat-content calorimeter was described previously.^{5/} Platinum-rhodium capsules, whose heat contents were determined in separate experiments, were used to hold the oxide samples. After the capsules were filled with the oxides, they were sealed gastight by platinum welding.

The heat contents are expressed in defined calories (1 calorie = 4.1840 absolute joules) per mole. Molecular weights were taken as 172.13 grams for cerium dioxide and 124.91 grams for columbium dioxide. The sample sizes were 15,690 grams of cerium dioxide and 8.673 grams of columbium dioxide (both corrected to vacuum).

The measured heat-content values are listed in table 1 and shown in figure 1. The precision uncertainty in these values is less than 0.2 percent.

TABLE 1. - Heat contents above 298.15° K. (measured values)

T, ° K.	H _T -H _{298.15} , cal./mole	T, ° K.	H _T -H _{298.15} , cal./mole	T, ° K.	H _T -H _{298.15} , cal./mole
CeO ₂					
400.6	1,575	897.7	10,330	1,397.1	19,850
500.6	3,230	1,002.5	12,310	1,498.5	21,890
595.7	4,860	1,099.3	14,130	1,598.3	23,860
697.2	6,680	1,196.8	16,010	1,696.8	25,860
799.9	8,530	1,302.1	18,000	1,798.3	27,930
CbO ₂					
399.3	1,460	1,078.9	14,710	1,259.3	18,630
500.5	3,060	1,084.4	14,800	1,300.1	19,530
598.7	4,710	1,089.1	15,040	1,396.8	21,430
699.1	6,460	1,100.5	15,340	1,396.9	21,360
800.3	8,330	1,101.8	15,330	1,447.1	22,390
899.0	10,250	1,108.5	15,470	1,497.9	23,440
1,000.7	12,520	1,124.0	15,800	1,597.1	25,420
1,001.7	12,510	1,150.7	16,440	1,697.8	27,380
1,050.2	13,760	1,199.1	17,480	1,790.8	29,500
1,069.9	14,380	1,199.1	17,430	-	-

The heat content of cerium dioxide is a regular function of temperature over the entire measured range (298.15° to 1,800° K.); no anomalous behavior

^{5/} Kelley, K. K., Naylor, B. F., and Shomate, C. H., The Thermodynamic Properties of Manganese: Bureau of Mines Tech. Paper 686, 1946, 34 pp.

FIGURE 1. - Heat Contents of Cerium Dioxide and Columbium Dioxide Above 298.15° K.

of any type was observed. The heat capacity increases from 14.73 calories per degree mole at 298.15° K. to 20.65 calories per degree mole at 1,800° K.

Columbium dioxide has two heat-content anomalies. The first occurs at 1,090° K. and appears to be the result of a maximum in the heat-capacity function. This anomaly is evident in figure 1. The second anomaly occurs at approximately 1,200° K. It appears as an abrupt change in heat capacity (that is, slope of the heat-content curve). It is not evident on a plot as small as figure 1 but may be seen readily on a larger plot. No isothermal heat absorption is associated with either anomaly. The heat capacity of columbium dioxide increases from 13.74 calories per degree mole at 298.15° K. to about 35 calories per degree mole at 1,090° K. It then decreases rapidly to 22.2 calories per degree mole, remains substantially constant to 1,200° K., and finally decreases abruptly to 19.85 calories per degree mole and remains substantially constant to 1,800° K.

Table 2 gives smooth values of the heat-content and entropy increments above 298.15° K. The latter were calculated from the former by the method of Kelley,^{6/} which assures that the values are mutually consistent.

TABLE 2. - Heat contents and entropies above 298.15° K.
(smooth values)

T,° K.	CeO ₂		CbO ₂	
	H _T -H _{298.15} , cal./mole	S _T -S _{298.15} , cal./deg. mole	H _T -H _{298.15} , cal./mole	S _T -S _{298.15} , cal./deg. mole
400	1,580	4.55	1,480	4.26
500	3,220	8.21	3,060	7.78
600	4,940	11.34	4,730	10.82
700	6,720	14.08	6,480	13.52
800	8,540	16.51	8,310	15.96
850	-	-	9,270	17.13
900	10,380	18.68	10,280	18.28
950	-	-	11,350	19.44
1,000	12,250	20.65	12,500	20.62
1,050	-	-	13,770	21.86
1,090	-	-	15,060(α)	23.06(α)
1,090	-	-	15,060(β)	23.06(β)
1,100	14,140	22.45	15,280	23.26
1,200	16,050	24.11	17,500(β)	25.20(β)
1,200	-	-	17,500(γ)	25.20(γ)
1,300	17,980	25.66	19,480	26.78
1,400	19,930	27.10	21,470	28.26
1,500	21,900	28.46	23,450	29.62
1,600	23,890	29.74	25,440	30.91
1,700	25,910	30.97	27,420	32.11
1,800	27,960	32.14	29,410	33.24

6/ Kelley, K. K., Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds: Bureau of Mines Bull. 584, 1960, 232 pp.

The heat-content values in table 2 are represented (with average deviations as indicated) by the following equations:

$\text{CeO}_2(\text{c}):$

$$H_T - H_{298.15} = 16.97T + 1.01 \times 10^{-3}T^2 + 2.54 \times 10^5T^{-1} - 6,001$$

(298° - 1,800° K.; 0.2 percent).

$\text{CbO}_2(\alpha):$

$$H_T - H_{298.15} = 11.70T + 4.78 \times 10^{-3}T^2 + 0.72 \times T^{-1} - 4,155$$

(298° - 950° K.; 0.5 percent),

($\Delta H_{1090} = 720$).

$\text{CbO}_2(\beta):$

$$H_T - H_{298.15} = 22.20T - 9,140 \quad (1,090^\circ - 1,200^\circ \text{ K.}; 0.2 \text{ percent}).$$

$\text{CbO}_2(\gamma):$

$$H_T - H_{298.15} = 19.85T - 6,320 \quad (1,200^\circ - 1,800^\circ \text{ K.}; 0.2 \text{ percent}).$$

It was impossible to fit the heat-content data for $\text{NbO}_2(\alpha)$ between 950° and 1,090° K. by the adopted type of equation. However, the given equation may be extrapolated to 1,090° K., provided that a heat increment of 720 calories per mole is added at 1,090° K. and treated in the same manner as if there were an isothermal heat absorption of this amount.

The corresponding heat-capacity equations are as follows:

$\text{CeO}_2(\text{c}):$

$$C_p = 16.97 + 2.02 \times 10^{-3}T - 2.54 \times 10^5T^{-2}.$$

$\text{CbO}_2(\alpha):$

$$C_p = 11.70 + 9.56 \times 10^{-3}T - 0.72 \times 10^5T^{-2}.$$

$\text{CbO}_2(\beta):$

$$C_p = 22.20.$$

$\text{CbO}_2(\gamma):$

$$C_p = 19.85.$$

DISCUSSION

No previous high-temperature heat-content data exist for columbium dioxide, and the two anomalies had not been reported. King^{7/} measured the heat capacity over the temperature range 51° to 298° K. The preceding high-temperature heat-capacity equation conforms with King's value at 298.15° K. (13.74 calories per degree mole).

Previous heat-content data for cerium dioxide extended to only 373° K. and comprised only three measurements made in 1880 and 1912. Kelley^{8/} has treated these data and adopted an average heat-capacity value of 15.1 calories per degree mole for the temperature interval 273° to 373° K. Calculation based upon the present measurements shows this value to be in error by less than 2 percent.

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^{7/} King, E. G., Low-Temperature Heat Capacities and Entropies at 298.15° K. of Some Oxides of Gallium, Germanium, Molybdenum, and Niobium: Jour. Am. Chem. Soc., vol. 80, 1958, p. 1799.

^{8/} Work cited in footnote 6 (p. 4).